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Submitted 7/23/65

SEMI-ANNUAL REPORT ON NASA NsG 314-63

I Summary

A description is given of the apparatus developed to investigate the effect of very high pressure on gases. Results on the melting curves of A, CO_2, NH_3 and CH_4 are given and evidence of solid-solid transitions in CO_2 and NH_3 is discussed. The experimental difficulties encountered are reviewed and the development of new equipment is also reported.

II Status of Experiments

A. Apparatus

The experiments thus far have been conducted in the piston-cylinder device shown in Figure 1. The tapered steel core (a) is interference fitted in steel binding rings for external support. The core is open at both ends with a static seal (b) placed at the top of the cylinder and the moving seal at the bottom actuated by the tungsten carbide piston (c). The piston in turn is moved by a 1000-ton hydraulic ram acting through long tension rods that enable the core and piston assembly to be immersed in the cryogenic coolant.

The gas is forced into the pressure chamber via the capillary tube usually after being pressurized to a working density by a separate intensifier. As the piston is raised the seal bypasses the capillary inlet thus reducing the possibility of a leak.

The entire core is brought to the appropriate temperature either by immersion in cold bath or by external heater. The piston is then advanced and any volume discontinuity encountered during melting or a solid-solid transition is detected by a micrometer gauge fixed to the tension rods. The piston is then lowered and the discontinuity is again detected on the release of pressure. A typical displacement curve is shown in Figure 2. The difference in the upstroke and downstroke gives the friction correction. The total friction in the 20 kb region is approximately 3 kb and the maximum variation in a corrected transition point between runs is approximately 1 kb.

The core can then be taken to another temperature and the process repeated to establish another point on the melting curve. In practice it is usually necessary to remove the piston and lower seal completely to replace the packings in the seals.

This arrangement has worked satisfactorily up to approximately 25 kb pressure but an excessive number of failures have been encountered above these pressures due to fracturing of the core. A new design has now been constructed (Figure 3) that features a larger binding ring system and large clamping nuts on either end of the core to give end-load support. This apparatus has now been assembled and preliminary trials have indicated that it will be satisfactory. The operating techniques are essentially the same as with the old core design.

B. Results

The melting curves determined to date are shown in Figures 4-7. The solid lines are established curves from previous workers in the field and the crossed circles mark the points determined in this study.

The curve for argon is shown in Figure 4 and the new points are in substantial agreement with the work of Lahr and Eversole (1962). There is no break in the melting curve, and none is expected because argon, like all other rare gases, crystallizes in cubic close-packed structure and no phase change is likely. No problems are anticipated in extending this curve to the 40 kb region, although the volume discontinuity on melting is relatively small.

The melting curve of CO_2 has been extended beyond Bridgman's (1914) data to 23 kb as shown in Figure 5. There is a very large and easily detected ΔV associated with the melting of this substance which descreases at higher pressure.

There is an indicating of a solid-solid transition at room temperature and approximately 25 kb. However, the ΔV is so small as to be within experimental error and therefore cannot as yet be definitely established. Bridgman (1938) has also suggested the possibility of a solid-solid transition in this pressure range in his compressibility studies.

Several preliminary experiments have been made to investigate electrical resistance variations in the solid CO_2 through the suspected transition region. However, these experiments have not yet proved successful due to difficulties in affecting a gas-tight insulated seal.

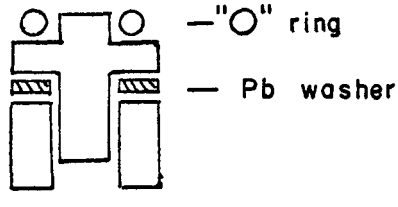
The melting curve of anhydrous ammonia has been extended to 16 kb from the previous limit of 3 kb reported by Vereshchagin and Voronov (1956). The melting curve as shown in Figure 6 has a definite break at approximately 5 kb and -40° C. This indicates a triple point with a solid-solid transition boundary in this region. Attempts to find this transition with the volume discontinuity apparatus have not been successful; however, preparations are now being made to determine the crystal structure of solid NH_3 in the 10 kb region by high pressure X-ray techniques. Inasmuch as the atmospheric pressure structure of this substance is a distorted face-centered cube, it is presumed the next high pressure will be an undistorted face-centered cube. There is also some evidence of another solid-solid transition at approximately 25 kb. An extension of the melting curve to this pressure region may help to substantiate this.

The only previous data on the melting curve of methane has been reported by Clusius and Weigand (1940) and their measurements extended to only 200 bars. The new melting points for this substance are plotted in Figure 7. The curvature of the melting curve is apparently normal in the region so far investigated but as Stewart (1959) has reported a solid-solid transition in the low temperature region, there is a distinct possibility that his I-III transition boundary may intersect the melting curve in the 15-20 kb region.

Again, since no volume discontinuity for this solid-solid transition has been detected, it is hoped that an extension of the melting curve will help resolve this region of the phase diagram.

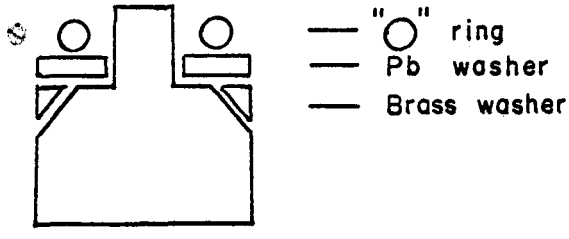
III Technical Difficulties

One of the primary difficulties with very high pressure gas research is the problem of sealing the gas both in its low pressure gaseous region and in the high pressure region where the gas is in its solid state. The problem is particularly accute for the moving seal. The solution of this problem has been to use a compound seal with both a soft "O" ring for low pressure sealing and a Bridgman "unsupported area" packing seal for the high pressure region. A schematic diagram of the seal is shown below.



The "O" rings must be chosen both for the temperature range of the experiment and for chemical compatibility with the substance under investigation. Butyl rubber, Si rubber and teflon "O" rings have been utilized extensively on all the experiments to date.

Unfortunately the Bridgman seal is susceptible to failure above 30 kb pressure. As other problems have prevented many excursions above 30 kb, this has not been a limiting factor as yet. However, several experiments with a wedge-shaped brass washer seal as shown below indicates a satisfactory solution has been found for a pressure seal for work in the maximum pressure range.



The use of lead or indium as backup washers for the "O" rings has been found not only to help insure a good seal but also helps reduce friction. The reduction of friction becomes increasingly important at higher pressure and/or lower temperatures.

It is anticipated that the problems of core failure as described in section II will not re-occur with the new core design. However, as higher pressures are obtained the problems of friction will most likely increase. This difficulty is also compounded by the fact that in general higher pressures result in lower volume discontinuities, thus increasing the uncertainties in determining a given phase boundary.

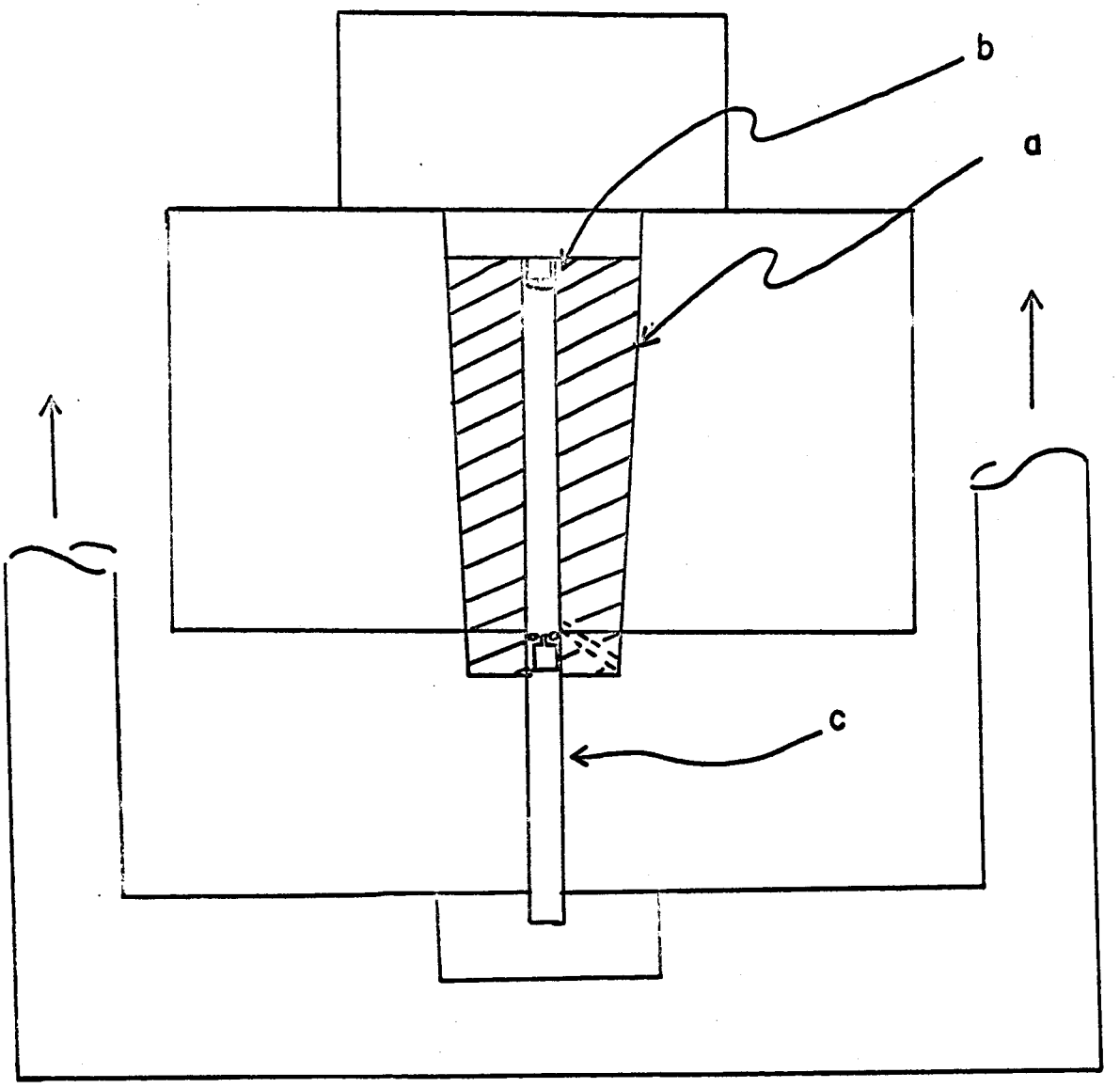
The capillary gas inlet proved to be critical. Initially the capillary tube was silver-soldered to the core but this proved to be a frequent source of leaks and has therefore been replaced by a cone-in-cone seal that is bolted on to the core. This has proved to be much more satisfactory.

IV References

1. Bridgman (1914) P. Am. Ac. Am. Sci.,v. 3, p. 153.
2. Bridgman (1938) P. Am. Ac. Am. Sci., v. 52, p. 91.
3. Clusius and Weigand (1940) Z. Phys. Chem., B 46, p. 1.
4. Stewart (1959) J. Phys. Chem. Solids, v. 12, p. 122.
5. Vershchagin and Voronov (1956) Zhur. Fix. Khim., v. 30, p. 329.

Fig. 1

Core Design



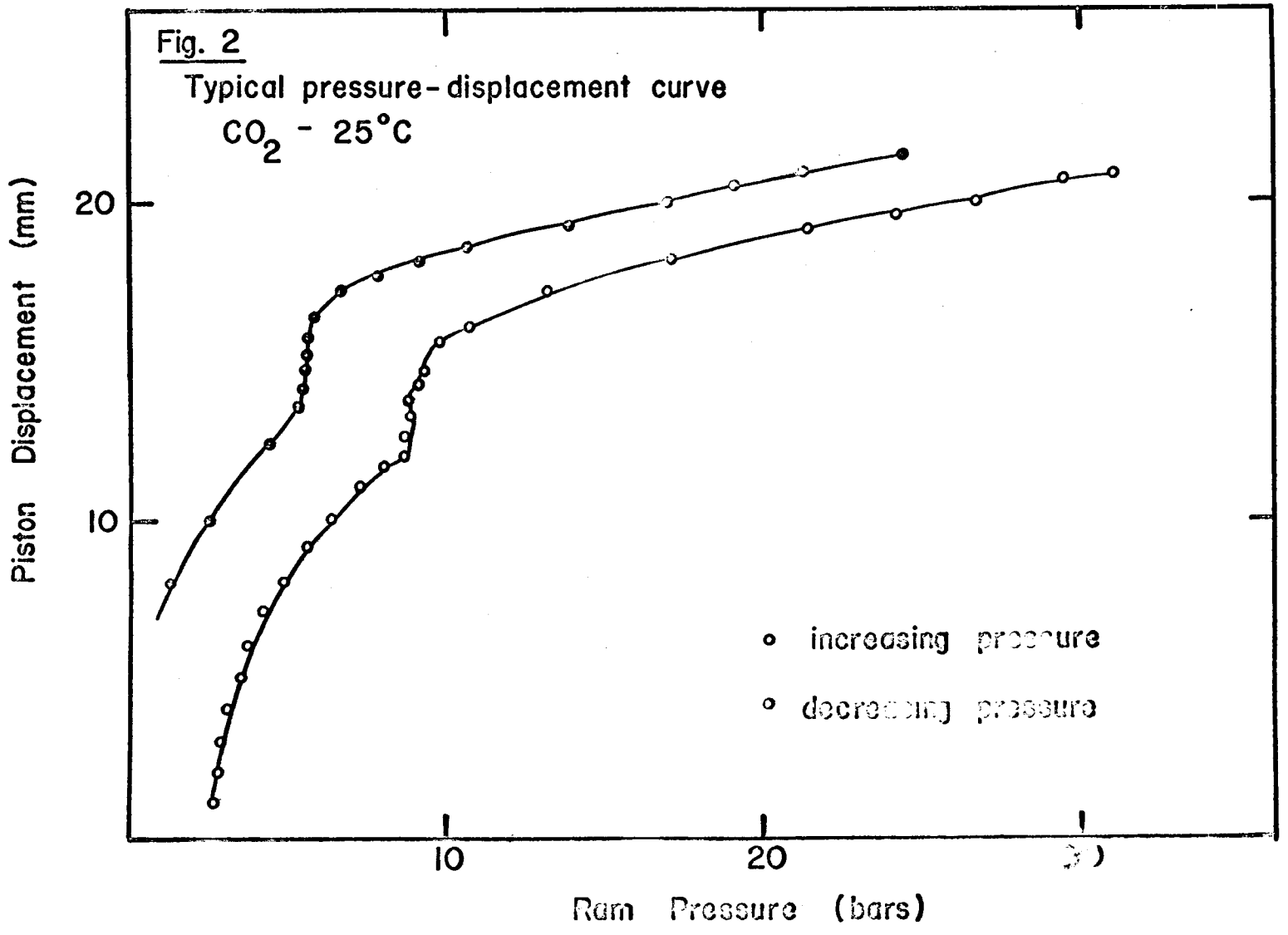
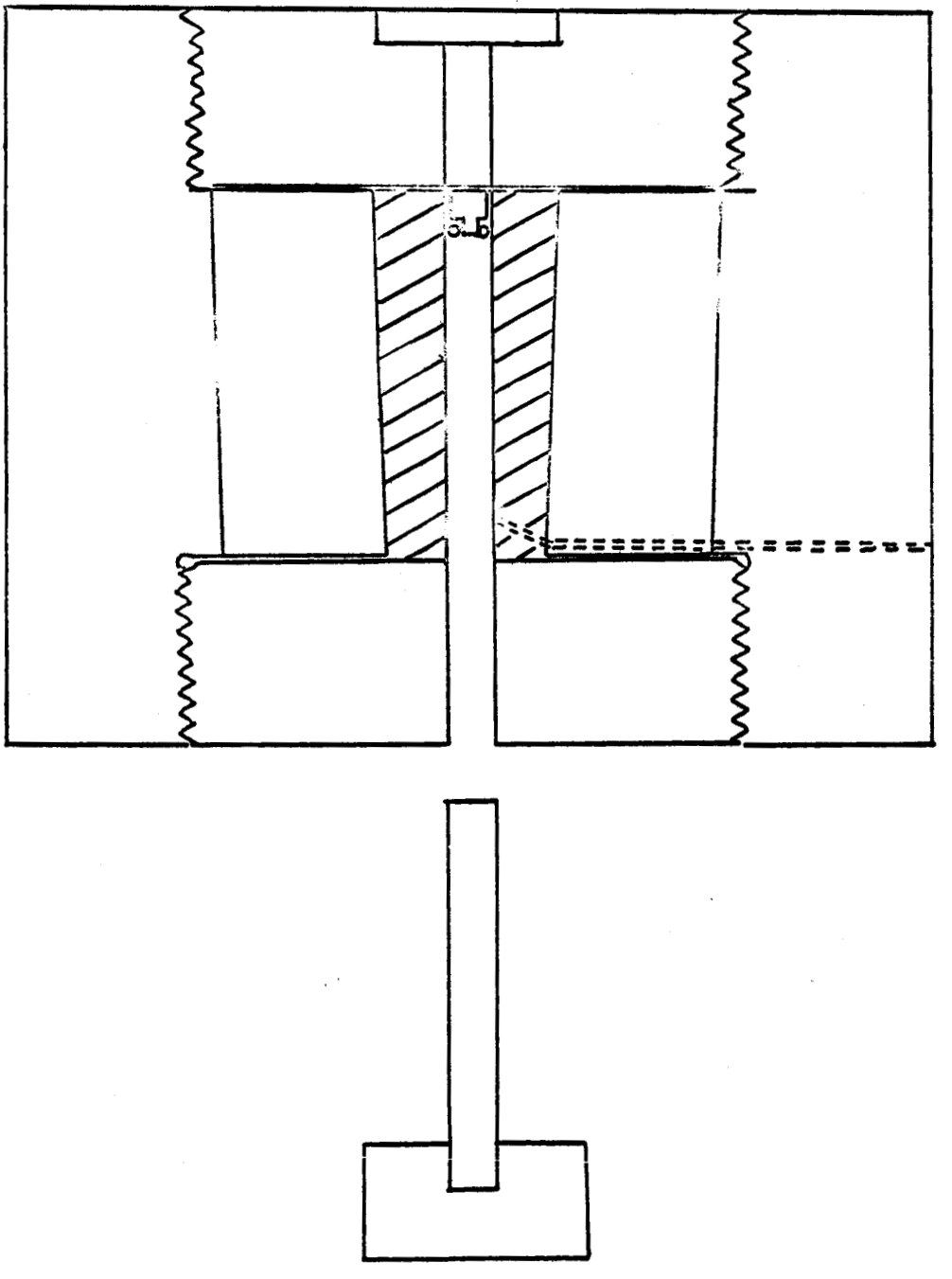


Fig. 2
Typical pressure-displacement curve
CO_2 - 25°C
Piston Displacement (mm)
20
10
increasing pressure
decreasing pressure
10
20
Ram Pressure (bars)

Fig. 3

End Loaded Core



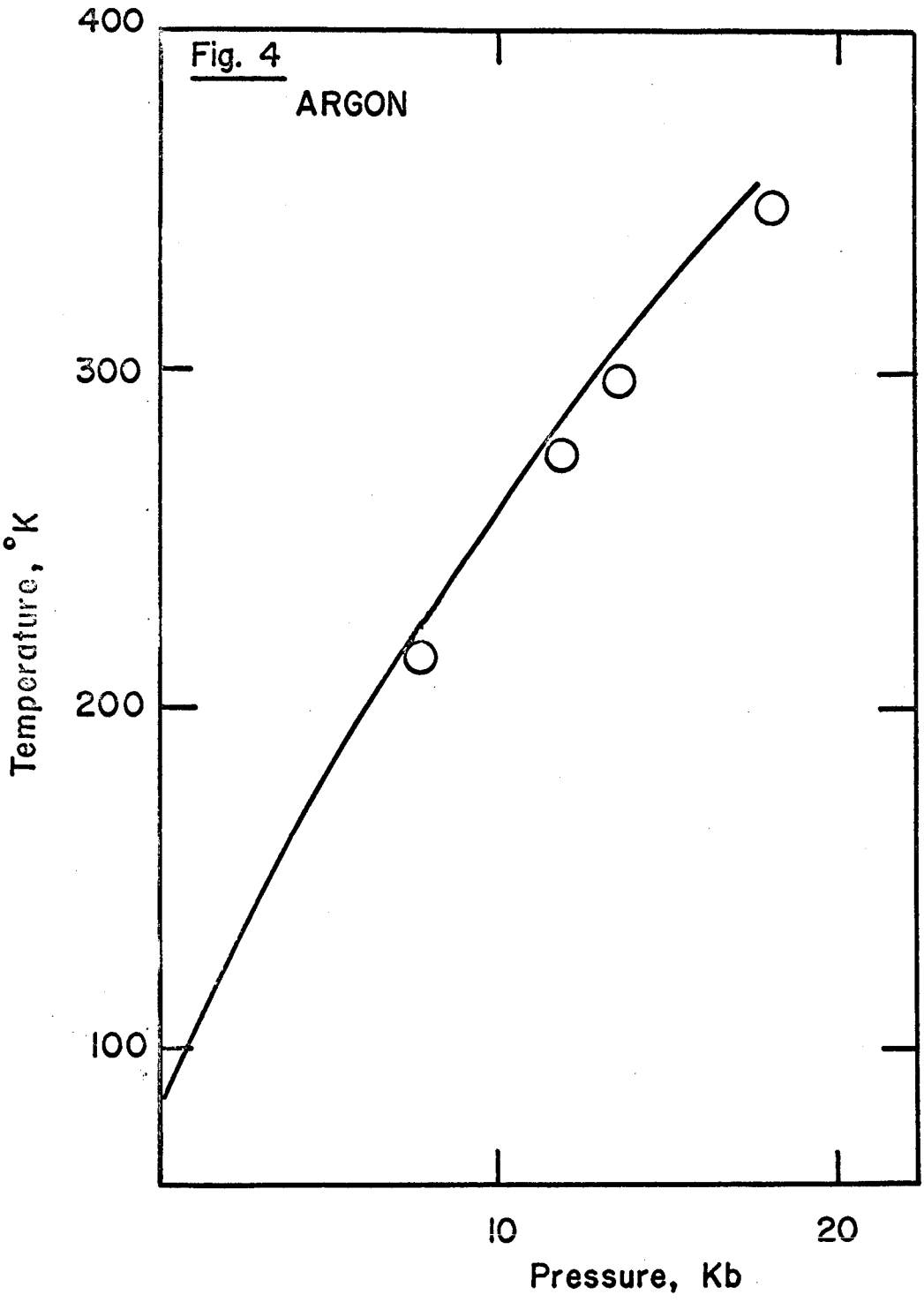


Fig. 4
ARGON
400
300
200
100
Temperature, °K
10
20
Pressure, Kb

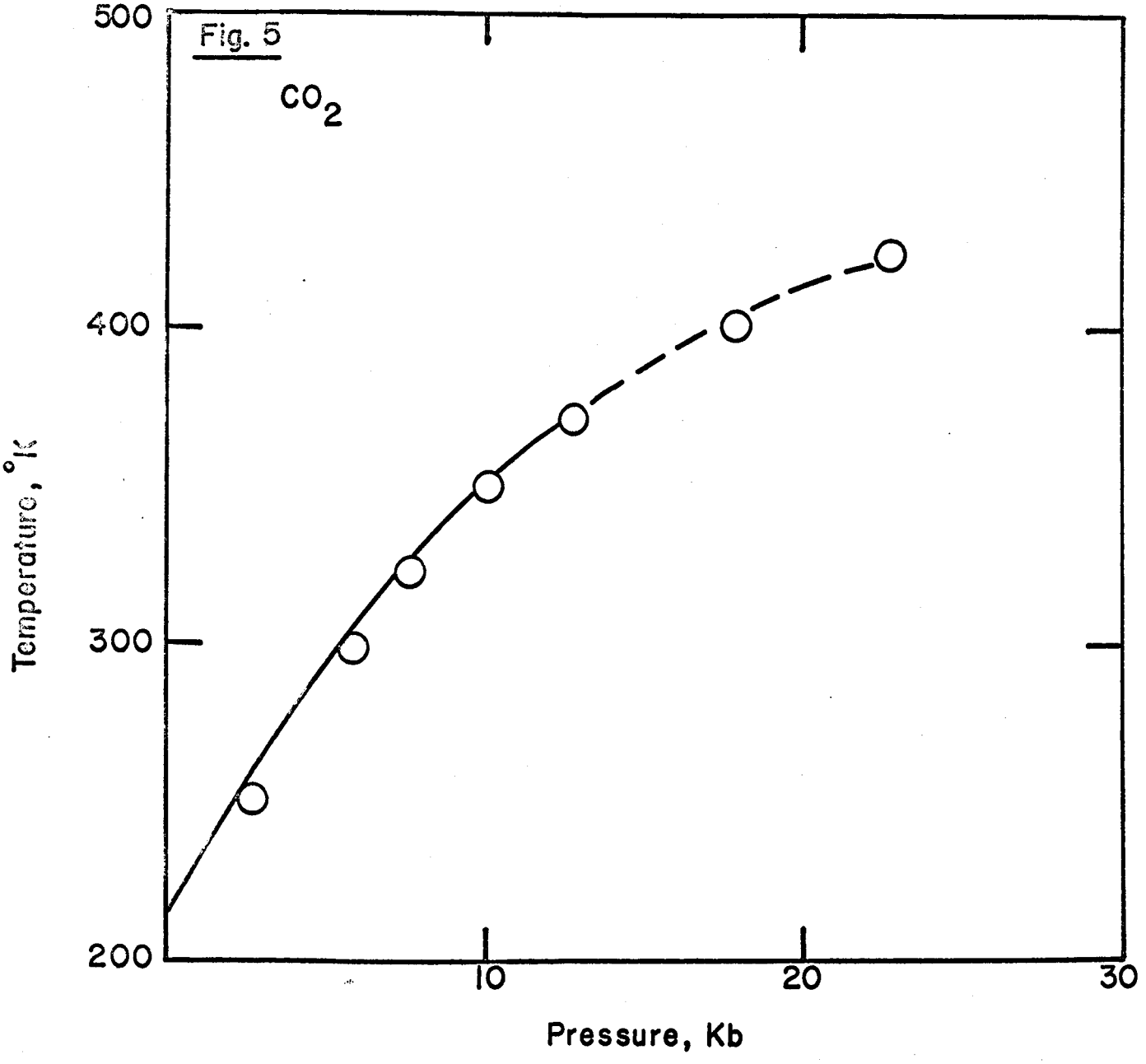


Fig. 5
CO_2
500
400
300
200
Temperature, °K
10
20
30
Pressure, Kb

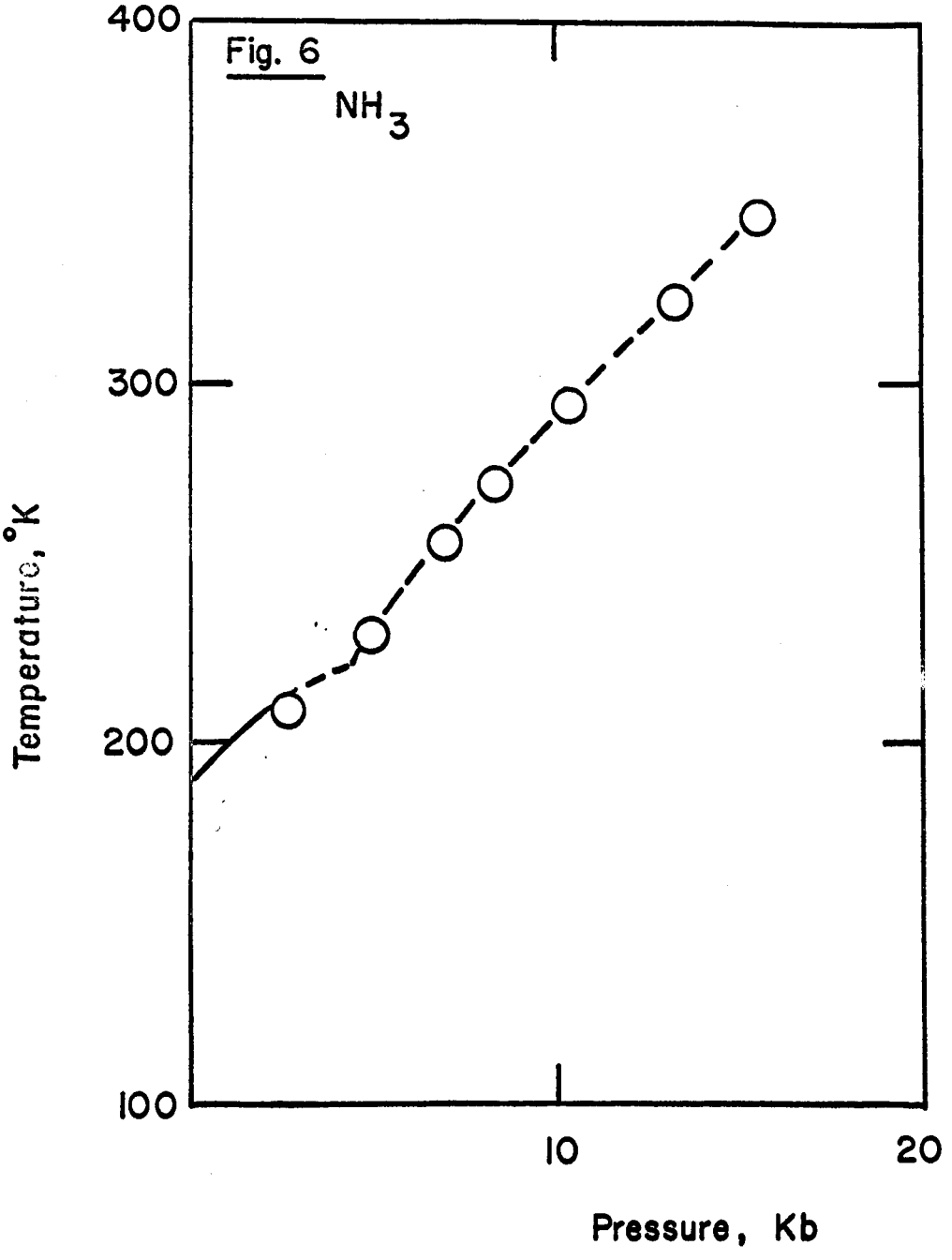


Fig. 6
NH3
400
300
200
100
Temperature, °K
10
20
Pressure, Kb

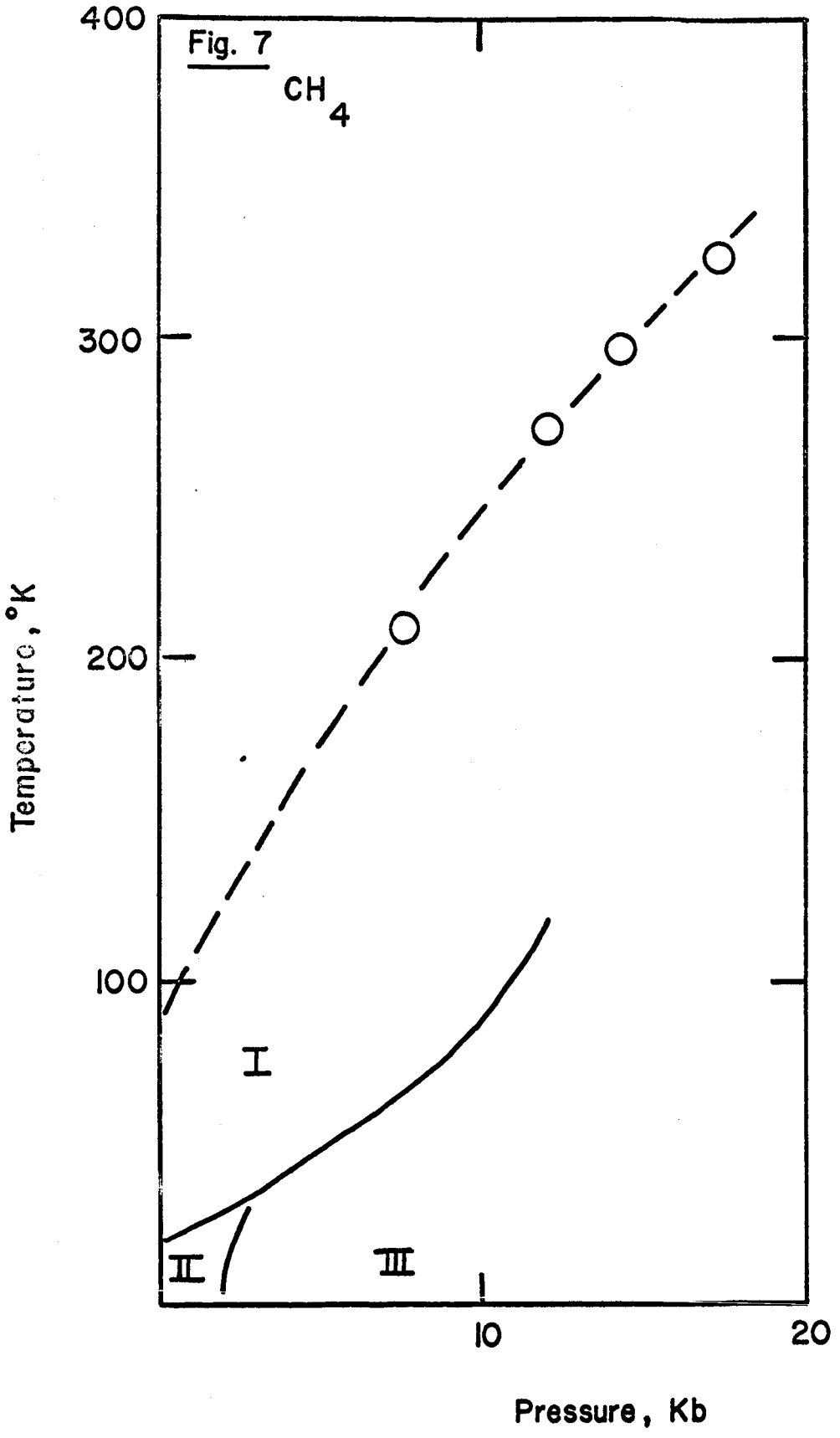


Fig. 7
CH4
400
300
200
100
Temperature, °K
I
II
III
10
20
Pressure, Kb